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Formation and Reactivity of the Osmium(IV) Cyanoimido Complex, $[Os^{IV}(bpy)(Cl)_3(NCN)]^-$

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Synthesis of [1A]: In a 100 mL round bottom flask, *trans*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ ($Os^{VI}\equiv N^+$) (200 mg, 0.306 mmol) was stirred in 50 mL CH_2Cl_2. One equivalent of NEt_4CN (47.8 mg) in 5 mL CH_2Cl_2 was added to the solution of $Os^{VI}\equiv N^+$. The reaction mixture was stirred for 10 min, and the brown precipitate was filtered, washed thoroughly with CH_2Cl_2, and air-dried. **[1B]** was prepared by a method similar to that used for **[1A]** except that *cis*-$[Os^{VI}(tpy)(Cl)_2(N)]^+$ was used as the starting material. **[1A]:** Yield: 148 mg (91 %). Anal. Calcd for $OsC_{16}H_{11}N_5Cl_2$: C, 35.96; H, 2.07; N, 13.11. Found: C, 36.17; H, 2.15; N, 13.32. UV-visible data (DMSO) λ_{max}, nm (ε, M^{-1} cm^{-1}): 870 (4.95×10^2), 521 (3.54×10^3), 421 (5.88×10^3), 318 (2.03×10^4), and 277 (2.08×10^4). Cyclic voltammetric data in 0.1 M TBAH/DMF (V versus SSCE): $E_{1/2}$(Os(VI/V)) = +1.72 V, $E_{1/2}$(Os(V/IV)) = +0.90 V, $E_{1/2}$ (Os(IV/III)) = -0.40 V, and $E_{1/2}$ (Os(III/II)) = -1.30 V. Infrared (cm^{-1}, nujol): $\nu(C\equiv N_\beta)$ = 1938 cm^{-1}; ν(tpy) 1466 (vs), 1456 (vs), and 1369 (vs). **[1B]:** Yield: 156 mg (95 %). Anal. Calcd for $OsC_{16}H_{11}N_5Cl_2$: C, 35.96; H, 2.07; N, 13.11. Found: C, 36.28; H, 2.21; N, 13.20. UV-visible

spectroscopic data in CH_3CN [λ_{max} (nm), $\varepsilon(M^{-1}\ cm^{-1})$]: 591 ($2.16 \times 10^3$), 415 ($6.56 \times 10^3$), 396 ($6.69 \times 10^3$), 314 ($2.20 \times 10^4$), 278 ($2.57 \times 10^4$), 273 ($2.57 \times 10^4$), 226 ($3.71 \times 10^4$), and 195 ($4.87 \times 10^4$). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$(Os(VI/V)) = +1.84 V, $E_{1/2}$(Os(V/IV)) = +0.99 V, $E_{1/2}$ (Os(IV/III)) = -0.32 V, and $E_{1/2}$ (Os(III/II)) = -1.32. Infrared (cm^{-1}, nujol): $\nu(C{\equiv}N_\beta)$ = 1934 cm^{-1}; ν(tpy) 1468 (vs), 1454 (vs), and 1367 (vs).

Synthesis of [2A]$^-$: In a 100 mL round bottom flask, [Os^{VI}(bpy)$(Cl)_3$(N)] ($Os^{VI}{\equiv}N$) (200 mg, 0.428 mmol) was stirred in 40 mL CH_3CN. One equivalent of NEt_4CN (47.8 mg) in 5 mL CH_3CN was added to the solution of $Os^{VI}{\equiv}N$. The reaction mixture was stirred for 20 min, and the brown solution was reduced to a small volume by rotary evaporation. Upon addition of Et_2O, the precipitated product was filtered and air-dried. Yield: 260 mg (97 %). Anal. Calcd for $OsC_{19}H_{28}N_5Cl_3{\bullet}CH_3CN$: C, 37.98; H, 4.71; N, 12.66. Found: C, 38.27; H, 5.10; N, 12.74. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), $\varepsilon(M^{-1}\ cm^{-1})$]: 510 ($4.66 \times 10^3$), 457 ($5.17 \times 10^3$), 297 ($2.04 \times 10^4$), 237 sh($1.53 \times 10^4$), and 199 ($3.31 \times 10^4$). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$(Os(VI/V)) = +1.87 V, $E_{1/2}$(Os(V/IV)) = +1.19 V, $E_{1/2}$ (Os(IV/III)) = +0.67 V, and $E_{1/2}$ (Os(III/II)) = -0.90. ^{1}H NMR (δ, CD_3CN): (4 H's, *d*) 12.78 $\rightarrow$ 12.76, 8.89 $\rightarrow$ 8.88, 6.30 $\rightarrow$ 6.27, -2.95 $\rightarrow$ -2.97; (4 H's, *dd*) 15.02 $\rightarrow$ 14.97, 8.78 $\rightarrow$ 8.75, 8.23 $\rightarrow$ 8.18, -1.71 $\rightarrow$ -1.76. Infrared (cm^{-1}, nujol): **^{14}N:** $\nu(C{\equiv}N_\beta)$ = 1975 cm^{-1}, ν(bpy) = 1601, 1566, 1043, 1026, 897, 769, and 648 cm^{-1}. **^{15}N:** $\nu(C{\equiv}N_\beta)$ = 1977 cm^{-1}, ν(bpy) = 1601, 1566, 1047, 1034, 895, 768, and 648 cm^{-1}.

Synthesis of [2B]: In a 100 mL erlenmeyer flask, $NEt_4[Os^{IV}(bpy)(Cl)_3(NCN)]$ (Os^{IV}=NCN^-) (200 mg, 0.321 mmol) was stirred in 5 mL CH_3CN. One equivalent of HPF_6 in 2 mL CH_3CN was added, and the reaction mixture was stirred for 10 min. The brown product was precipitated upon addition of 20 mL H_2O. Yield: 142 mg (90 %). Anal. Calcd for $OsC_{11}H_9N_4Cl_3 \bullet 2H_2O$: C, 24.94; H, 2.47; N, 10.56. Found: C, 25.18; H, 2.67; N, 10.59. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 550 sh (4.43×10^3), 495 (4.78×10^3), 461 (4.74×10^3), 427 (4.88×10^3), 293 (2.04×10^4), 222 (2.34×10^4), and 199 (3.31×10^4). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$(Os(VI/V)) = 1.17 V, $E_{1/2}$(Os(V/IV)) = 0.65 V, $E_{1/2}$ (Os(IV/III)) = -0.47 V, and $E_{1/2}$ (Os(III/II)) = -1.04. ^{1}H NMR (δ, CD_3CN): (4 H's, *d*) 9.09 → 9.07, 8.71 → 8.68, 8.41 → 8.38, 8.37 → 8.36; (4 H's, *dd*) 8.64 → 8.61, 8.35 → 8.23, 7.86 → 7.81, 7.62 → 7.57. Infrared (cm^{-1}, nujol): **^{14}N:** ν(N-H) = 3230 cm^{-1}; $\nu(C{\equiv}N_\beta)$ = 2187 cm^{-1}, ν(bpy) = 1605, 1566, 1043, 1026, 897, 769, and 648 cm^{-1}. **^{15}N:** ν(N-H) = 3213 cm^{-1}; $\nu(C{\equiv}N_\beta)$ = 2181 cm^{-1}, ν(bpy) = 1601, 1566, 1047, 1034, 895, 768, and 648 cm^{-1}.

Synthesis of [2C]$^+$: it was prepared by a method similar to that used for **[2B]** except that at least 2 equivalents of HPF_6 were used. Yield: 187 mg (91 %). Anal. Calcd for $OsC_{11}H_{10}N_4Cl_3PF_6 \bullet H_2O$: C, 20.09; H, 1.84; N, 8.52. Found: C, 20.27; H, 2.05; N, 8.74. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 460 (4.48×10^3), 428 (5.15×10^3), 292 (2.24×10^4), 238 sh (1.30×10^4), and 210 (2.29×10^4). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V

versus SSCE): $E_{1/2}$ (Os(IV/III)) = 0.97 V and $E_{1/2}$ (Os(III/II)) = -0.87. Infrared (cm^{-1}, nujol): **^{14}N:** ν(N-H) = 3332 cm^{-1} and 3200; ν($N_{\alpha}\equiv C$) = 2280 cm^{-1}, ν(bpy) = 1605, 1564, 1049, 1036, 897, 771, and 646 cm^{-1}. **^{15}N:** ν(N-H) = 3336 cm^{-1}, 3197 cm^{-1}, ν($N_{\alpha}\equiv C$) = 2249 cm^{-1}; ν(bpy) = 1605, 1566, 1047, 1034, 893, 773, and 648 cm^{-1}; and ν(P-F) = 845 cm^{-1}.

Synthesis of [3]$^{+}$: In a two-necked, round bottom flask, $[Os^{IV}(bpy)(Cl)_3(NCN)]^{-}$ (Os^{IV}=NCN^{-}) (200 mg, 0.321 mmol) was stirred in 50 mL CH_2Cl_2 under a nitrogen atmosphere for 10 min. Two equivalents of $[Et_3O]BF_4$ in 5 mL CH_2Cl_2 was bubbled with nitrogen for 3 min, and added drop wise into the solution of Os^{IV}=NCN^{-} through a pressure equalizing dropping funnel. The reaction mixture was stirred continuously under nitrogen for 3 hrs. The brown solution mixture was evaporated to 10 mL by rotary evaporation. The precipitated product was filtered, washed thoroughly with CH_2Cl_2, and air-dried. Yield: 182 mg (89 %). Anal. Calcd for $OsC_{15}H_{18}N_4Cl_3BF_4 \bullet ½Et_2O$: C, 30.26; H, 3.44; N, 8.30. Found: C, 30.52; H, 3.58; N, 8.51. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 484 (2.58×10^3), 458 sh (2.47×10^3), 372 (4.55×10^3), 330 sh (6.51×10^3), 294 (1.87×10^4), 218 sh (2.11×10^4), and 200 (2.16×10^4). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$ (Os(IV/III)) = 0.79 V and $E_{1/2}$ (Os(III/II)) = -0.63. Infrared (cm^{-1}, nujol): **^{14}N:** ν($^{14}N_{\alpha}\equiv C$) = 2206 cm^{-1}; ν(bpy) = 1607, 1566, 1040, 1026, 893, 771, and 656 cm^{-1}; and ν(B-F) = 1076 cm^{-1}. **^{15}N:** ν($^{15}N_{\alpha}\equiv C$) = 2176 cm^{-1}.

Synthesis of [4]$^{+}$: it was prepared by a method similar to that used for **[3]$^{+}$** except that 2 equivalents of MeI were

used in CH_3CN solvent. Yield: 182 mg (85 %). Anal. Calcd for $OsC_{13}H_{14}N_4Cl_3PF_6 \bullet 1½CH_3CN$: C, 26.35; H, 2.56; N, 10.56. Found: C, 26.01; H, 2.61; N, 10.75. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 494 (2.00×10^3), 422 sh (1.89×10^3), 358 sh (3.83×10^3), 328 sh (5.21×10^3), 294 (1.67×10^4), 246 (1.44×10^4), and 210 (1.82×10^4). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$ (Os(IV/III)) = 0.74 V and $E_{1/2}$ (Os(III/II)) = -0.58. Infrared (cm^{-1}, nujol): **^{14}N:** $\nu(^{14}N_\alpha{\equiv}C)$ = 2202 cm^{-1}; ν(bpy) = 1607, 1566, 1040, 1026, 893, 771, and 656 cm^{-1}; and ν(P-F) = 843 cm^{-1}. **^{15}N:** $\nu(^{15}N_\alpha{\equiv}C)$ = 2173 cm^{-1}.

Synthesis of [5]$^+$: it was prepared by a method similar to that used for [**3**]$^+$ except that [**2B**] was used as the starting material, and 1 equivalent of acetic anhydride ($(MeCO)_2O$) was used in *N*,*N*-dimethylformamide (DMF) solvent. [**5**]$^+$ was further recrystallized from a mixture of $CH_3CN \bullet HPF_6/Et_2O$. Yield: 216 mg (78 %). Anal. Calcd for $OsC_{13}H_{12}N_4Cl_3OPF_6 \bullet CH_3CN$: C, 24.92; H, 2.09; N, 9.69. Found: C, 24.94; H, 2.15; N, 9.72. UV-visible spectroscopic data in CH_3CN [λ_{max} (nm), ε (M^{-1} cm^{-1})]: 547 (2.38×10^3), 294 (1.15×10^4), 276 (8.15×10^3), 268 (7.26×10^3), 260 (6.97×10^3), and 207 (4.03×10^4). Cyclic voltammetric data in 0.1 M TBAH/CH_3CN (V versus SSCE): $E_{1/2}$ (Os(IV/III)) = +0.84 V and $E_{1/2}$ (Os(III/II)) = -0.55. Infrared (cm^{-1}, nujol): **^{14}N:** ν(N-H) = 3329 cm^{-1}; $\nu(N_\alpha{\equiv}C)$ = 2208 cm^{-1}; ν(C=O) = 2628 cm^{-1}; ν(bpy) = 1606, 1539, 1047, 1034, 889, 770, and 648 cm^{-1}; and ν(P-F) = 841 cm^{-1}. **^{15}N:** $\nu(^{15}N_\alpha{\equiv}C)$ = 2179 cm^{-1}.

Structure Analysis of [2A]$^-$: Crystals of $NEt_4[Os^{IV}(tpy)(Cl)_2(NCN)]$ were grown by vapor diffusion of Et_2O into a

CH_3CN solution of the salt. They are triclinic, space group P-1, with a = 9.6473(4) Å, b = 10.0130(5) Å, c = 13.5767(6) Å, α = 87.717(1) °, β = 83.557(1) °, γ = 82.610(1) °, V = 1291.95(10) $Å^3$, Z = 2, fw = 664.07, d_{calc} = 1.707 g/cm^3, and μ = 5.26 mm^{-1}. Intensity data were collected at -100 °C on a Siemens CCD SMART Diffractometer with Mo Kα radiation and a graphite monochromator by using the ω scan mode. A total of 8194 reflections were collected, and 3985 of them were unique. 3586 reflections with $I > 2.5\ \sigma(I)$ were used in the structure refinement by full-matrix least-squares techniques (281 parameters). Absorption corrections were made by using SADABS. Final R_f = 5.9 %, R_w = 7.2 %, GoF = 2.4544 (R = 6.2 %, R_w = 7.2 %, for all reflections). NRCVAX was used as the software package. Crystallographic data (excluding structure factors) for NEt_4[**2A**] in this communication have been deposited with the Cambridge Crystallographic Data Center as supplementary publication number CCDC-158913. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44) 1223-336-033, e-mail: deposit@ccdc.cam.ac.uk).

Figure Caption

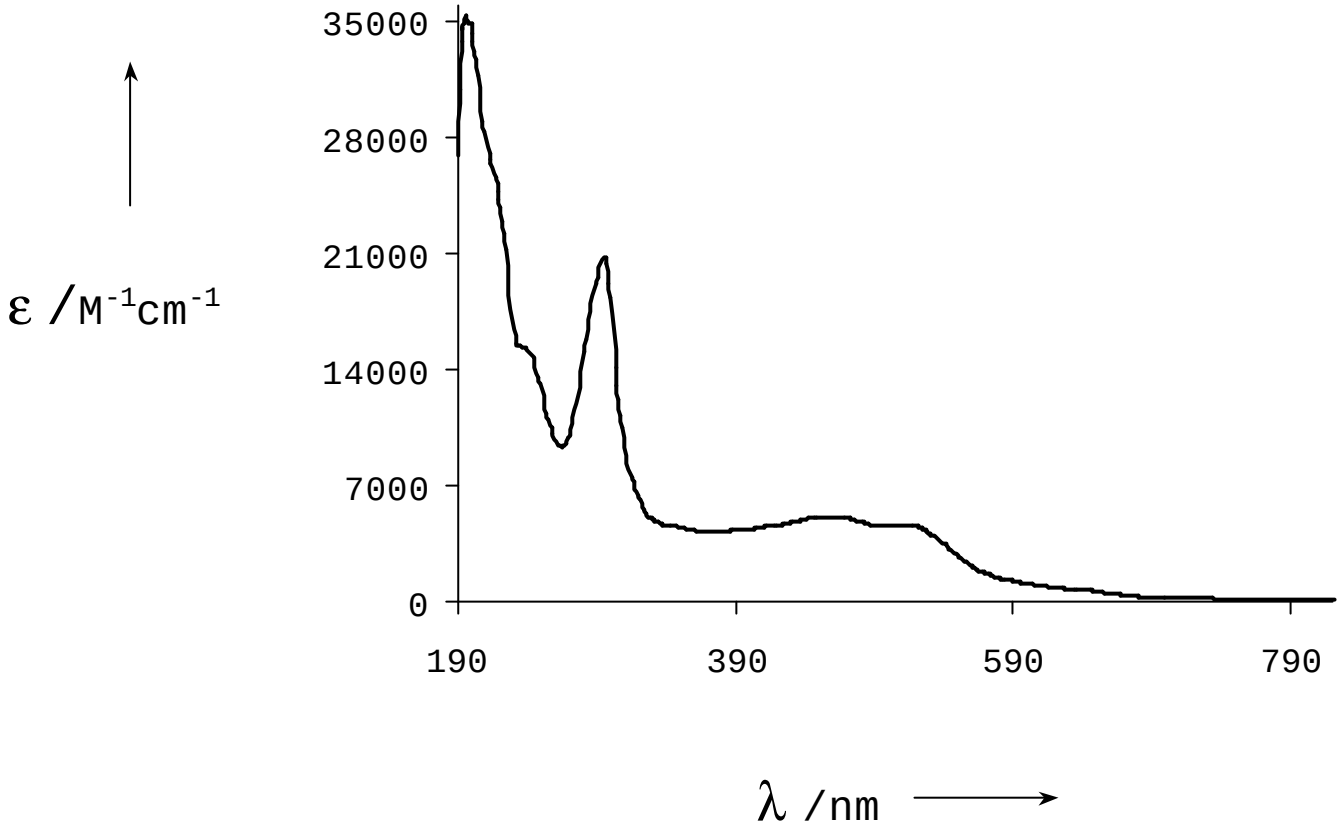
Supporting Information Figure 1. The effect of protonation on electronic absorption spectra in CH_3CN for:

A) $NEt_4[Os^{IV}(bpy)(Cl)_3(N_\alpha\text{-}C\equiv N_\beta)]$ ([**2A**]$^-$),

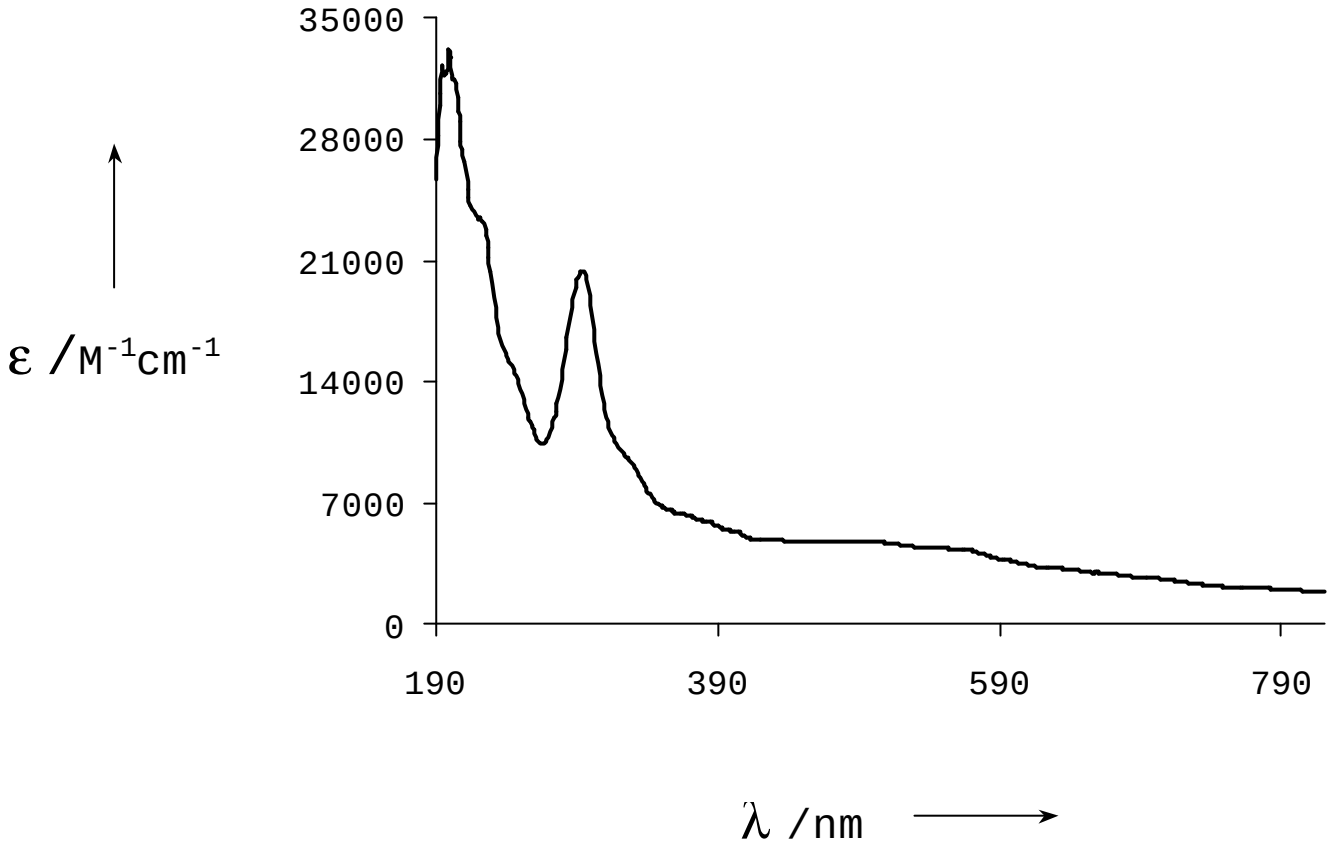
B) $[Os^{IV}(bpy)(Cl)_3(N_\alpha(H)\text{-}C\equiv N_\beta)]$ ([**2B**]), and

C) $[Os^{IV}(bpy)(Cl)_3(N_\alpha\equiv C\text{-}N_\beta H_2)](PF_6)$ ([**2C**]$^+$)

Supporting Information Figure 1A



Supporting Information Figure 1B



Supporting Information Figure 1C